Graft Polymerization on Magnetic Polymer Substrates*

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Synopsis

Functional monomers were graft polymerized onto substrates consisting of magnetic iron oxides in a crosslinked PVA matrix. Initiation was carried out with H_2O_2 and $FeSO_4$; other common chemical initiating systems proved unsuccessful. Peroxide treatment of the substrates must be carried out separately from the reaction with Fe^{2+} and monomer. The amount of grafting achieved is highly variable, depending on the nature of the monomer. Strong base and weak acid magnetic shell resins prepared by graft polymerization are useful in water treatment by flocculation and moving-bed ion exchange, respectively. A wider range of products can be obtained by chemical modification of grafted chains. The mechanism of grafting is discussed in an endeavor to explain the highly specific nature of the reaction.

INTRODUCTION

Ion exchange resins having high reaction rates and convenient handling properties can be made by forming a shell of resin about a magnetic core. Such particles flocculate strongly when magnetized, so that very fine beads have settling rates comparable with those of much larger nonmagnetic beads, yet agitation will disrupt the flocs and allow the fine particles to react extremely rapidly with the surrounding electrolyte medium. Beds of magnetic resin have a very high void water content, enabling the resin to be pumped continuously in moving-bed plant without damage.[1,2] Strong base magnetic resins are extremely effective in flocculating colloidal clay, algae, and color-causing dissolved organics in river water and wastewater effluents.

Magnetic ion exchange resins can be made by graft polymerization of the appropriate monomer on a composite substrate consisting of a magnetic material embedded in a polymer matrix. Grafting of a precursor monomer followed by chemical modification enables a wider range of exchange resins to be produced.

This paper is concerned with graft polymerization, initiated by H_2O_2 and $FeSO_4$, on substrates consisting of magnetic iron oxides in a matrix of poly(vinyl alcohol) (PVA) nominally 100% crosslinked with glutaraldehyde. A variety of monomers has been used and widely varying levels of grafting achieved.† Analogous graft copolymers have been prepared in the past using gamma irradiation techniques.[3]

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† The methods employed are the subject of a patent application: B. A. Bolto, D. R. Dixon, and R. J. Eldridge (to CSIRO/I.C.I. Australia Limited) Australian Pat. Appl. PC 8692. Commercial development of the magnetic materials and treatment processes is being undertaken by I.C.I. Australia Limited.

EXPERIMENTAL

Grafting was carried out by a two-step procedure. Five-gram lots of the magnetic core were stirred with 10–15 ml of **100 volume** H_2O_2 solution for 10–15 min, then washed free of excess H_2O_2. The peroxidized core was then added to an aqueous solution of the monomer and $FeSO_4$ and stirred for 30–180 min. Free access of air was allowed throughout and was found to be essential prior to addition of the monomer and $FeSO_4$. Weak base monomers were used in the hydrochloride form. At the end of the reaction the products were filtered off and washed with distilled water. Acid and basic resins were passed through several ion exchange cycles and again washed.

No grafting resulted if the H_2O_2 and $FeSO_4$ were added together. Other transition metal–H_2O_2 systems, Ce(IV), and $K_2S_2O_8$ also gave no graft. Attempts to graft from nonaqueous solutions were also unsuccessful.

The extent of grafting of acid monomers was determined by adding a known excess of NaOH and back titrating. The apparent capacity decreased somewhat during the preliminary washing and cycling steps. In use there was a further slight decline at first, then the capacity remained constant over some hundreds or thousands of cycles.[2] This behavior suggests that trapped homopolymer is gradually removed, leaving only chemically grafted polyacid. The shell graft structure of the products is confirmed by their much faster reaction with $NaHCO_3$ solution in comparison to conventional ion exchange resins.[1]

Base resins were analyzed by acid–base titration or by eluting the chloride form with excess $NaNO_3$ and titrating with standard $AgNO_3$ solution. In the case of nonionic monomers the increase in mass was a sufficiently accurate indicator of the extent of grafting. Microanalysis of some products provided a check on the titration and gravimetric methods.

RESULTS

Effect of Concentration

The yield of graft copolymer increases with increasing monomer concentration, as shown for acrylamide in Figure 1. The suggestion of a maximum in the curve for the smaller $FeSO_4$ concentration can be attributed to the viscosity increase resulting from homopolymerization. There is an optimum $FeSO_4$ concentration for any monomer, as shown for acrylamide in Figure 2. This optimum is independent of monomer concentration and corresponds to a reduction in homopolymerization, which generally accompanies grafting.

Effect of Monomer

The maximum capacity obtained with each monomer and the corresponding concentration of $FeSO_4$ are shown in Table I. An easily polymerized monomer such as acrylic acid gives capacities up to 7.0 meq/g. The acrylic acid graft has been prepared on a large scale (starting from 4 kg of core) and has been used for dealkalization of hard, alkaline waters on a pilot scale (60 m³/day).[4] Another application which has been demonstrated on a laboratory scale is the removal of heavy metals from effluents.[5]

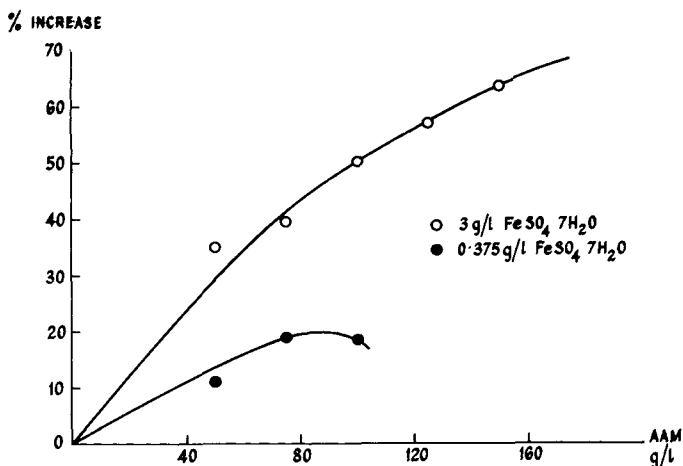Methacrylic acid (MAA) gives lower capacities than acrylic, and its behavior

Fig. 1. Effect of monomer concentration on amount of acrylamide grafted to magnetic PVA beads.
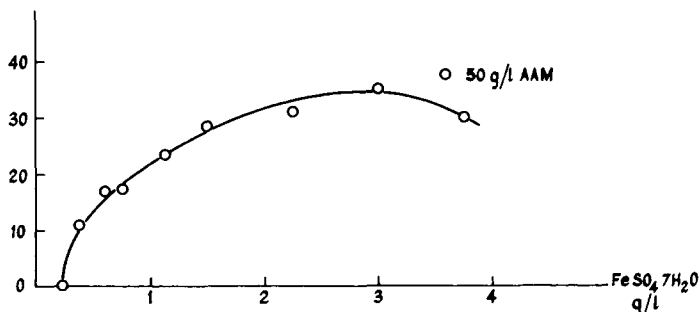

Fig. 2. Effect of Fe^{2+} concentration on amount of acrylamide grafted to magnetic PVA beads. Acrylamide concentration 50 g/1.

is erratic. In particular, the MAA reaction is very sensitive to stirring conditions. In the 5-g scale experiments, stirring at 75 rpm gives a capacity of 1.5 meq/g, but varying the rate up or down by 25 rpm decreases the capacity by about 50%.

The four sulfonic monomers listed in Table I all fail to graft, yielding homopolymer only. Attempts to cograft these monomers with acrylic acid gave grafts of acrylic acid only. The formation of homopolymer, and the fact that no grafting occurs even in the presence of added electrolyte, suggest that the failure of these monomers to graft is not an electrostatic effect. This conclusion is confirmed by the reasonably high yields obtained with quaternary ammonium monomers (Table I).

Of the nonionic monomers, acrylamide grafts nearly as well as acrylic acid, while vinyl acetate, which was grafted from a three-phase system, gives much lower yields. This can be attributed to the low water solubility (2 g/100 ml) of vinyl acetate, if it is postulated that only monomer dissolved in the aqueous phase grafts. The still lower level of grafting obtained with vinylbenzyl chloride (VBC), which is soluble to only 7 mg/100 ml, is consistent with this postulate.

The results obtained with 4-vinylpyridine (4VP) seem to be anomalous. Although the products had quite high capacities when first isolated, the capacities rapidly declined on treatment with 0.3M NaOH solution. This behavior is in-

TABLE I

Monomer	Capacity, meq/g	FeSO$_4$· 7H$_2$O, g/l.
Acrylic acid (AA)	7.0	3.0
Methacrylic acid (MAA)	2.5	5.6
Sodium vinylsulfonate	0	
Sodium 2-sulfoethyl acrylate	0	
Sodium 2-sulfoethyl methacrylate	0	
2-Acrylamido-2-methylpropanesulfonic acid (AMPS)	0	
2-Dimethylaminoethyl methacrylate	0.14	
2-Dimethylaminopropylacrylamide	0.15	0.38
2-Vinylpyridinium chloride (2VP)	0.05	
4-Vinylpyridinium chloride (4VP)	1.1	1.5
2-Methyl-5-vinylpyridinium chloride (2M5VP)	0.04	
1-Ethyl-4-vinylpyridinium p-toluenesulfonate	0.5	
2-Hydroxy-3-methacrylyloxypropyltrimethylammonium chloride	1.1	0.75
2-Methacrylyloxyethyltrimethylammonium methyl sulfate	0.8	3.0
Acrylamide	6.3	3.0
Vinyl acetate	2.6	
Vinylbenzyl chloride (VBC)	0.2	

consistent with the expected poly(vinylpyridine) structure and suggests that the grafted chains contain the ionene structure known to form during spontaneous polymerization of 4VP.[6–13] However, spontaneous polymerization leads to this structure only at a higher pH level than was used during the grafting experiments. High monomer concentrations also do not favor ionene formation.[8,10,11] According to Kabanov's group,[8] a mixed structure of the type
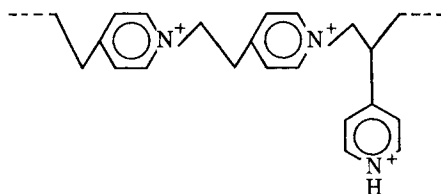
is formed in the pH range of 0.5–1. However, 4VP grafts were labile even when prepared at pH<0. The reason for this lability remains uncertain.

2-Vinylpyridine (2VP) and 2-methyl-5-vinylpyridine (2M5VP) will spontaneously polymerize in acid media, but neither forms a high molecular weight ionene polymer.[14–18] Both these monomers gave much lower yields of graft than did 4VP.
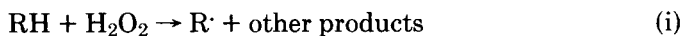
Modification of Graft Copolymers

Acrylic acid grafts have been partly esterified with isethionic acid, water being removed by azeotropic distillation. However, the degree of esterification did not exceed 50%. Attempts to prepare derivatives via acyl chloride intermediates were unsuccessful, but AA grafts can be readily converted to strong base derivatives by reaction with glycidyltrimethylammonium chloride. Reaction in one step with epichlorohydrin and diethylamine gives weak base derivatives.
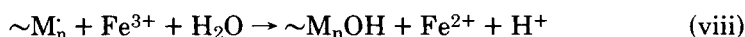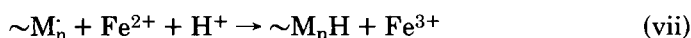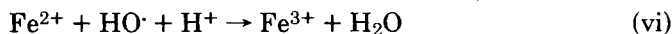
Vinyl acetate grafts are completely hydrolyzed by reaction with $1-2M$ NaOH solution at room temperature, but hydrolysis of acrylamide grafts does not proceed beyond 50%. Acrylamide grafts have been converted in moderate yield to amines by treatment with excess NaOCl at room temperature. Higher yields of an amine derivative can be obtained from the Mannich reaction with formaldehyde and diethylamine, but the product is very readily hydrolyzed.

DISCUSSION

The H_2O_2–Fe(II) system has been widely used to initiate graft copolymerization to substrates such as starch, cellulose, and soluble PVA. However, the two components of the initiator are invariably added together. Our finding that grafting occurs only when the peroxide treatment is separated from the addition of Fe(II) and monomer appears to be unique, although the reaction with O_2 parallels the sequence used in gamma irradiation procedures.[19] We envisage a mechanism involving formation of radical sites on the substrate in the first step, followed by reaction with O_2 to form peroxy radicals which then react with Fe^{2+}, probably forming alkoxy radicals:

$$RH + H_2O_2 \rightarrow R\cdot + \text{other products} \tag{i}$$

$$R\cdot + O_2 \rightarrow RO_2^{\cdot} \tag{ii}$$

$$RO_2^{\cdot} + Fe^{2+} + H^+ \rightarrow RO\cdot + Fe^{3+} + HO\cdot \tag{iii}$$

Possible subsequent reactions include

$$RO\cdot + nM \rightarrow ROM_n^{\cdot} \tag{iv}$$

$$HO\cdot + nM \rightarrow HOM_n^{\cdot} \tag{v}$$

$$Fe^{2+} + HO\cdot + H^+ \rightarrow Fe^{3+} + H_2O \tag{vi}$$

$$\sim M_n^{\cdot} + Fe^{2+} + H^+ \rightarrow \sim M_nH + Fe^{3+} \tag{vii}$$

$$\sim M_n^{\cdot} + Fe^{3+} + H_2O \rightarrow \sim M_nOH + Fe^{2+} + H^+ \tag{viii}$$

$$RH + OH\cdot \rightarrow R\cdot + H_2O \tag{ix}$$

$$HOM_n^{\cdot} + RO\cdot \rightarrow ROM_nOH \tag{x}$$

where M represents monomer.

Reaction (i) is almost certainly catalyzed by traces of iron compounds leached from the magnetic cores. Hydrogen peroxide is known not to oxidize organic compounds such as amylopectin in the absence of transition metal or similar catalysts.[20] Stirring 5 g magnetic core in 25 ml of 100 volume H_2O_2 for 30 min gives an Fe concentration in the supernate of ca. 4 mg/l. (by atomic absorption). Blank cores containing no added iron oxide will graft only small amounts of acrylic acid when subjected to the usual grafting procedure.

The Fe^{2+} ion is thus involved in initiation, reactions (i)–(iii), termination (vii), and suppression of homopolymerization (vi). This is consistent with the findings that the yield passes through a maximum, while the amount of homopolymer decreases (although not necessarily to zero) as the Fe^{2+} concentration in the second step is increased.

The stability of the graft linkage is fairly high, but slow loss of capacity in use

has been observed. This seems to be consistent with an ether link as shown in reaction (iv). No evidence exists for any of reactions (viii)–(x), but they may contribute to at least a small extent.

The failure of other initiating systems and of some monomers to give any graft, and the variation of the optimum Fe^{2+} concentration, indicate that grafting efficiency depends on the mixed potential of the monomer–initiator–substrate redox system. The failure of VBC to graft from nonaqueous solvents can also be explained in these terms. Further work is required to elucidate the details of the relation between redox potential and graft yield.

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